

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) EP 0 999 239 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
10.05.2000 Bulletin 2000/19

(51) Int Cl.7: C09B 57/14, C09B 57/08

(21) Application number: 99811010.0

(22) Date of filing: 04.11.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• Kaul, Bansil Lal
4105 Blie-Benken (CH)
• Plastra, Bruno
68330 Huningue (FR)
• Graclet, Jean Christoph
68330 Huningue (FR)

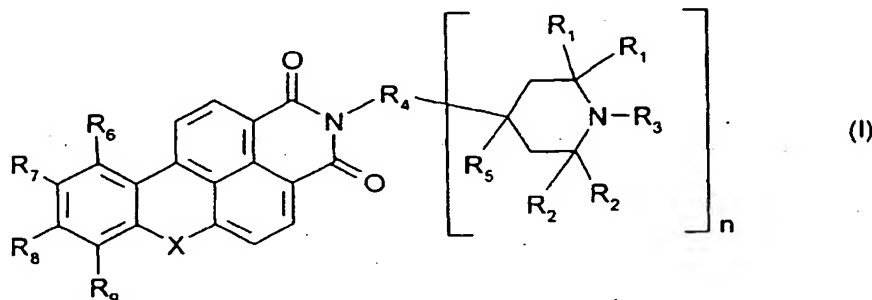
(30) Priority: 06.11.1998 GB 9824314

(71) Applicant: Clarlant Finance (BVI) Limited
Road Town, Tortola (VG)

(74) Representative: D'haemer, Jan Constant
Clarlant International Ltd.,
Rothausstrasse 61
4132 Muttenz 1 (CH)

(54) Heterocyclic compounds

(57) Compounds of the formula (I)



in which the substituents are as defined in claim 1
are valuable colorants for the mass coloring of polymers, with fluorescence property, in electrophotographics toners
and developers, in powders coating materials and ink-jet inks.

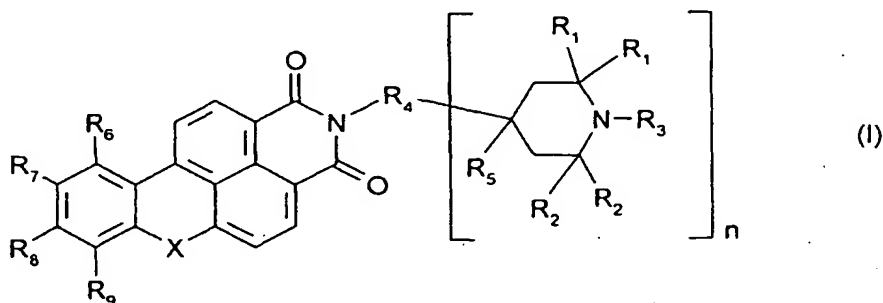
Description

[0001] The present invention relates to novel colorants for the mass coloring of polymers. In the mass coloring of polar polymers in particular, examples being polyamides, polyesters, polycarbonates and ABS, stringent requirements in terms of their heat stability and light fastness are expected from the dyes used.

[0002] The object of the present invention is, therefore, to provide heat-stable, light-fast and readily polymer-soluble colorants, with fluorescence property.

[0003] It has been found that the compounds of the formula (I) defined below achieve the stated object.

[0004] The invention provides a compound of the formula (I)



in which

each R₁
each R₂
R₃

independently is -CH₃ or -CH₂(C₁₋₄alkyl) or both groups R₁ form a group -(CH₂)₅;
independently is -CH₃ or -CH₂(C₁₋₄alkyl) or both groups R₁ form a group -(CH₂)₅;
is hydrogen, C₁₋₆alkyl, C₃₋₁₀alkenyl, phenyl, phenyl-C₁₋₄alkyl or -COR_{5a} where R_{5a} is hydrogen,
-C(R_{10a})=CH₂, C₁₋₆alkyl, phenyl, -COOC₁₋₄alkyl or -NR₂₁R₂₂, where R_{10a} is hydrogen or C₁₋₄
alkyl; R₂₁ is hydrogen, C₁₋₁₂alkyl, C₅₋₆cycloalkyl, phenyl, phenyl-C₁₋₄alkyl or C₁₋₁₂alkylphenyl
and R₂₂ is hydrogen or C₁₋₁₂alkyl;

R₄

is a direct bond or a bridging group; and

R₅

is hydrogen or C₁₋₄alkyl; or

R₄ and R₅

together with the carbon atom to which they are attached form an isocyclic or heterocyclic
bridging group;

R₆, R₇, R₈ and R₉

are independently hydrogen, halogen, R₁₁R₁₂N-, R₁₂-O- or R₁₂-S-, in which R₁₂ is C₁₋₆-alkyl,
C₆-C₁₀-aryl, (C₆-C₁₀)-aryl-(C₁₋₆)-alkyl or (C₁₋₆)-alkyl-(C₆-C₁₀)-aryl, in which the alkyl and/
or aryl radicals can be substituted by hydroxyl, C₁₋₆-alkoxy, C₆-C₁₀-aryloxy or halogen;

X

is sulphur, oxygen or N-R₁₁, in which R₁₁ is hydrogen, C₁₋₆-alkyl, C₆-C₁₀-aryl, (C₆-C₁₀)-aryl-
(C₁₋₆)-alkyl or (C₁₋₆)-alkyl-(C₆-C₁₀)-aryl, it being possible for the alkyl and/or aryl radicals
to be substituted by hydroxyl, C₁₋₆-alkoxy, C₆-C₁₀-aryloxy or halogen;

n

is an integer from 1 to 4 inclusive.

[0005] Preferred compounds of the formula (I) are those in which each R₁ and each R₂ is methyl.

[0006] Compounds of the formula (I) which are also preferred are those in which R₃ is hydrogen, methyl, ethyl, C₁₋₄alkylcarbonyl or C₂₋₄alkenylcarbonyl, more preferably hydrogen.

[0007] R₄ as a bridging group is preferably -NHCOphenyl-, -NHSO₂phenyl- with the phenyl group bonded to the nitrogen atom of the heterocyclic system.

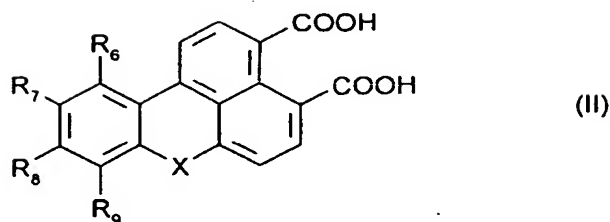
[0008] Compounds of the formula (I) which are also preferred are those in which R₅ is hydrogen.

[0009] Preference is also given to compounds of the formula (I) in which R₆, R₇, R₈, R₉ are independently hydrogen, chlorine, bromine, methoxy, ethoxy, phenoxy, -NH-C₆H₄-OCH₃, -O-C₆H₄-OCH₃ or -S-C₆H₄-OCH₃.

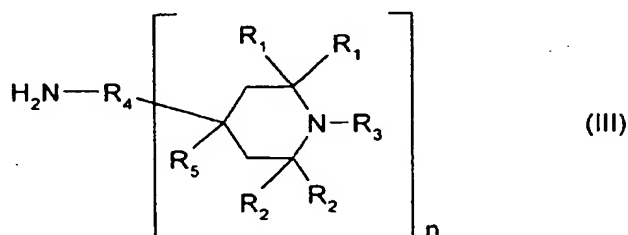
[0010] X is preferably sulphur and n is preferably 1 or 2.

[0011] Particular preference is given to compounds of the formula (I) in which R₁ and R₂ are methyl and R₃ and R₅ are hydrogen and R₄ is a direct bond.

[0012] The present invention also provides a process for preparing the compounds of the formula (I), characterized in that a dicarboxylic acid of the formula (II)



10
or, preferably, one of its functional derivatives, e.g. the acid anhydride or acid halide, is condensed with an amine or the salt of an amine of the formula (III)



25
[0013] Examples of suitable salts of the amine of the formula (III) are the chlorohydrate or the sulphate.

[0014] Condensation takes place in a molar ratio of (II):(III) of from 1: 3 to 3:1.

30 [0015] Condensation can be conducted without solvent in the melt at temperatures, for instance, of between 150°C and 300°C, preferably up to 250°C, or in an inert solvent at temperatures between 25°C and 300°C, preferably between 100°C and 250°C, in the presence or absence of a catalyst, at atmospheric pressure or under pressure.

35 [0016] Examples of suitable solvents are relatively high-boiling aliphatic or aromatic, substituted or unsubstituted hydrocarbons, examples being xylene (mixture), biphenyl, nitrobenzene, chlorobenzenes, chloronaphthalene, glycol ethers, organic acids and acid amides, especially dimethylformamide, dimethylacetamide or N-methyl-pyrrolidone. If the dicarboxylic acid of the formula (II) is employed in the form of the free acid it is also possible to use water or a relatively high-boiling alcohol, such as ethylene glycol, as solvent.

[0017] Examples of possible catalysts are inorganic or organic acids, such as hydrochloric or sulphuric acid, benzenesulphonic, toluenesulphonic acid, or acetic acid. The salts of organic acids, such as sodium or potassium acetate, are in many cases also suitable as catalysts.

40 [0018] The compounds of the invention are eminently suitable for the coloring of melts of synthetic polar polymers such as, for example, ABS, polyester, polycarbonate or polyamides. Polyamides are, for example, polycondensation products or addition polymerization products of dicarboxylic acids and diamines, e.g. of adipic acid and hexamethylenediamine, of lactams, e.g. ε-caprolactam, or of aminocarboxylic acids, e.g. ω-aminoundecanoic acid. The polyamide melt mixed with the pigment is brought into its final form by conventional methods - for example, in melt spinning, injection molding, extrusion or film blowing machines.

45 [0019] Some of the novel dyes of formula (I) give a fluorescent coloration in synthetic polar polymers such as, for example, ABS, polyester, polycarbonate or polyamides.

[0020] The novel dyes of the formula (I) are extremely stable to the heat stress which is necessarily part of the coloring of synthetic polyamides, and the substrates mass-colored with them also display excellent fastness properties, especially light fastness. Their high polymer-solubility is particularly noteworthy.

50 [0021] The novel compounds of the formula (I) are also suitable as colorants in electrophotographic toners and developers, such as one- or two-component powder toners (also called one- or two-component developers), magnetic toners, liquid toners, polymerization toners and specialty toners (literature: L.B. Schein, "Electrophotography and Development Physics"; Springer Series in Electrophysics 14, Springer Verlag, 2nd Edition, 1992).

55 [0022] Typical toner binders are addition polymerization, polyaddition and polycondensation resins, such as styrene, styrene-acrylate, styrene-butadiene, acrylate, polyester and phenol-epoxy resins, polysulphones, polyurethanes, individually or in combination, and also polyethylene and polypropylene, which may comprise further constituents, such as charge control agents, waxes or flow assistants, or may be modified subsequently with these additives.

[0023] The novel compounds of the formula (I) are suitable, furthermore, as colorants in powders and powder coating materials, especially in triboelectrically or electrokinetically sprayable powder coating materials which are used for the surface coating of articles made, for example, from metal, wood, plastic, glass, ceramic, concrete, textile material, paper or rubber (J.F. Hughes, "Electrostatics Powder Coating" Research Studies, John Wiley & Sons, 1984).

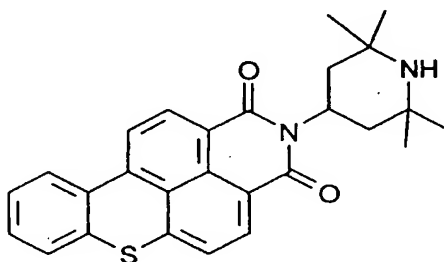
[0024] Powder coating resins that are typically employed are epoxy resins, carboxyl- and hydroxyl-containing polyester resins, polyurethane resins and acrylic resins, together with customary hardeners. Combinations of resins are also used. For example, epoxy resins are frequently employed in combination with carboxyl- and hydroxyl-containing polyester resins. Typical hardener components (as a function of the resin system) are, for example, acid anhydrides, imidazoles and also dicyanodiamide and its derivatives, blocked isocyanates, bisacylurethanes, phenolic and melamine resins, triglycidyl isocyanurates, oxazolines and dicarboxylic acids.

[0025] In addition, the novel compounds of the formula (I) are suitable as colorants in ink-jet inks, both aqueous and non-aqueous, and in those inks which operate in accordance with the hotmelt process.

[0026] In the examples below, parts are by weight.

EXAMPLE 1

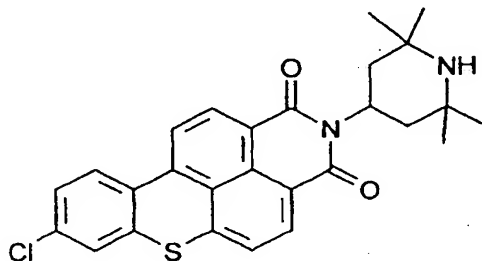
[0027] 30.4 parts of benzo[k,l]thioxanthene-3,4-dicarboxylic anhydride are suspended in 170 parts of N,N-dimethylacetamide. 17.2 parts of 4-amino-2,2,6,6-tetramethylpiperidine and 0.3 parts of para-toluenesulfonic acid are then added to the suspension, and then heated at 140°C for 6 hours. The suspension is then cooled to 100°C and filtered. The cake is washed with hot dimethylacetamide, warm water and dried. This gives 24.7 parts of an orange-colored powder.



When applied in PA-6, this compound gives a very bright yellow fluorescent transparent color.

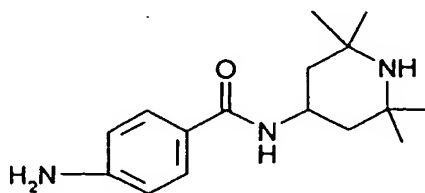
EXAMPLE 2

[0028] 10 parts of 9-chloro-benzo[k,l]thioxanthene-3,4-dicarboxylic anhydride are suspended in 80 parts of N,N-dimethylacetamide. 14 parts of 4-amino-2,2,6,6-tetramethylpiperidine and 0.5 parts of para-toluenesulfonic acid are then added to the suspension, and then heated at reflux for 24 hours. The suspension is then cooled to 25°C and filtered. The cake is washed with dimethylacetamide, alcohol and dried. This gives 10 parts of an orange-colored powder.

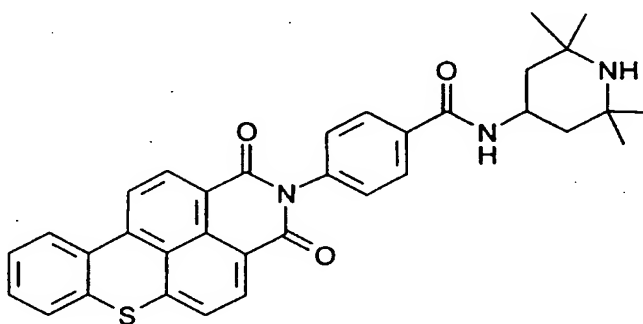


EXAMPLE 3

[0029] 16.7 parts of benzo[k,l]thioxanthene-3,4-dicarboxylic anhydride are suspended in 150 parts of N,N-dimethylacetamide. 15.15 parts of the following amine



and 0.1 parts of *para*-toluenesulfonic acid are then added to the suspension, and then heated at reflux for 24 hours. The suspension is then cooled to 25°C and filtered. The cake is washed with dimethylacetamide, alcohol and dried. This gives 22.8 parts of an orange-colored powder.



[0030] The dyes listed in Table 1 below are prepared in analogy to Example 3.

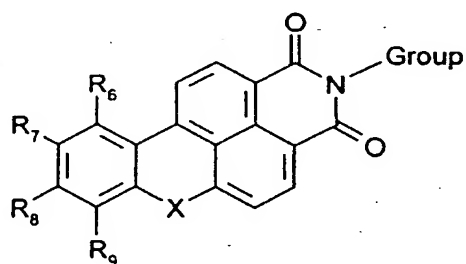
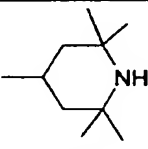
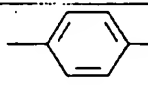
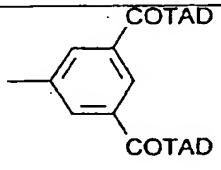
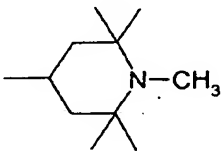
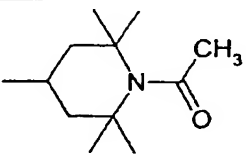
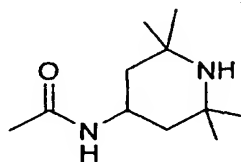


TABLE 1

Ex.No.	X	R ₆	R ₇	R ₈	R ₉	Group	Shade in nylon 6.6
4	S	H	H	CH ₃	H		Yellow
5	S	H	H	OCH ₃	H	ditto	Yellow
6	S	H	H	CF ₃	H	ditto	Yellow
7	O	H	H	H	H	ditto	Yellow
8	O	H	H	Cl	H	ditto	Yellow
9	NEthyl	H	H	H	H	ditto	Orange
10	S	H	H	Cl	H	 -COTAD	Yellow

11	S	H	H	H	H		Yellow
12	S	H	H	H	H		Yellow
13	S	H	H	H	H		Yellow



where -COTAD means:

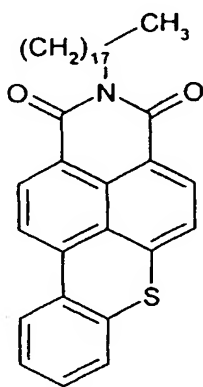
USE EXAMPLE

[0031] 100 parts of polycaprolactam in the form of a powder are mixed with 0.1 and with 1.0 part respectively of the dye from Example 1 in powder form in a drum mixer. After a short time, the powder is uniformly distributed and adheres to the granules. After about 10 minutes, the mixture is dried at 120°C for 16 hours, transferred to a melt spinning machine and following a residence time of about 8 minutes is spun to fibers at 275-280°C under a nitrogen atmosphere. The yellow-colored fibers are extremely lightfast.

[0032] All other known synthetic polyamides (nylon, Perlon, etc.) can be mass-colored in the same way, as can polyesters, ABS and polycarbonates, using the compounds of examples 1 to 13.

APPLICATION EXAMPLE

[0033] Polyester fibers containing 0.5% (w/w) of the colorant described in the example 1 have been prepared and compared against polyester fibers containing 0.5% (w/w) of the S.Y. 98 having the formula

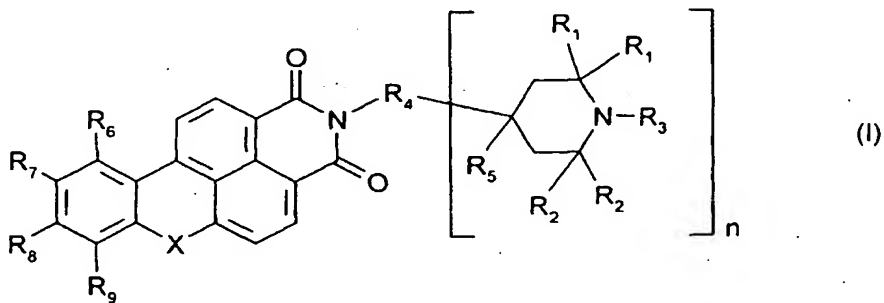


according to the following method:

[0034] The polyester is fused and extruded through a drawing plate at constant rate by gears pump regulation. The spinning machine is heated during 2 hours at temperatures of 260°C, 262°C, 262°C, 265°C and 265°C under pressure of 80 bars. The drawing plate is heated in an oven at 350°C for at least 30 minutes. The obtained fibers are recovered on a bobbin. The fibers colored with our product give a bright fluorescent yellow color with 15% higher color strength compared to S.Y. 98. Light and weather fastness are excellent.

Claims

1. Compound of the formula (I)



in which

each R_1
each R_2
 R_3

independently is $-\text{CH}_3$ or $-\text{CH}_2(\text{C}_{1-4}\text{alkyl})$ or both groups R_1 form a group $-(\text{CH}_2)_5-$;
independently is $-\text{CH}_3$ or $-\text{CH}_2(\text{C}_{1-4}\text{alkyl})$ or both groups R_1 form a group $-(\text{CH}_2)_5-$;
is hydrogen, $\text{C}_{1-8}\text{alkyl}$, $\text{C}_{3-10}\text{alkenyl}$, phenyl, phenyl- $\text{C}_{1-4}\text{alkyl}$ or $-\text{COR}_{5a}$ where R_{5a} is hy-
drogen, $-\text{C}(\text{R}_{10a})=\text{CH}_2$, $\text{C}_{1-6}\text{alkyl}$, phenyl, $-\text{COOC}_{1-4}\text{alkyl}$ or $-\text{NR}_{21}\text{R}_{22}$, where R_{10a} is hy-
drogen or $\text{C}_{1-4}\text{alkyl}$; R_{21} is hydrogen, $\text{C}_{1-12}\text{alkyl}$, $\text{C}_{5-6}\text{cycloalkyl}$, phenyl, phenyl- $\text{C}_{1-4}\text{alkyl}$
or $\text{C}_{1-12}\text{alkylphenyl}$ and R_{22} is hydrogen or $\text{C}_{1-12}\text{alkyl}$;

R_4
 R_5
 R_4 and R_5

is a direct bond or a bridging group;
is hydrogen or $\text{C}_{1-4}\text{alkyl}$; or
together with the carbon atom to which they are attached form an isocyclic or heterocyclic
bridging group;

R_6 , R_7 , R_8 and R_9

are independently hydrogen, halogen, or $\text{R}_{11}\text{R}_{12}\text{N}-$, or $\text{R}_{12}\text{-O-}$ or $\text{R}_{12}\text{-S-}$, in which R_{12} is
 $\text{C}_1\text{-C}_6\text{-alkyl}$, $\text{C}_6\text{-C}_{10}\text{-aryl}$, $(\text{C}_6\text{-C}_{10})\text{-aryl}(\text{C}_1\text{-C}_6)\text{-alkyl}$ or $(\text{C}_1\text{-C}_6)\text{-alkyl}(\text{C}_6\text{-C}_{10})\text{-aryl}$, in
which the alkyl and/or aryl radicals can be substituted by hydroxyl, $\text{C}_1\text{-C}_6\text{-alkoxy}$, $\text{C}_6\text{-C}_{10}\text{-aryloxy}$ or halogen.

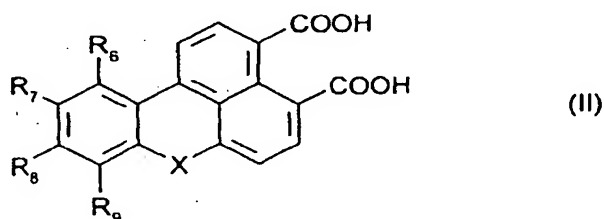
X

is sulphur, oxygen or N-R_{11} , in which R_{11} is hydrogen, $\text{C}_1\text{-C}_6\text{-alkyl}$, $\text{C}_6\text{-C}_{10}\text{-aryl}$, $(\text{C}_6\text{-C}_{10})\text{-aryl}(\text{C}_1\text{-C}_6)\text{-alkyl}$ or $(\text{C}_1\text{-C}_6)\text{-alkyl}(\text{C}_6\text{-C}_{10})\text{-aryl}$, it being possible for the alkyl and/or aryl
radicals to be substituted by hydroxyl, $\text{C}_1\text{-C}_6\text{-alkoxy}$, $\text{C}_6\text{-C}_{10}\text{-aryloxy}$ or halogen;

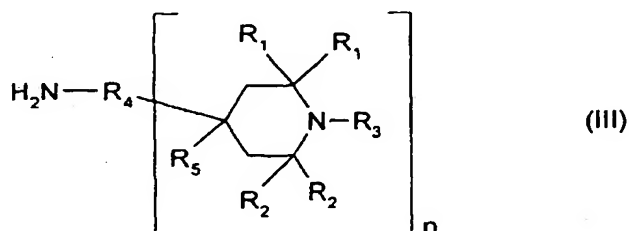
n

is an integer from 1 to 4 inclusive.

2. Compound according to Claim 1, characterized in that R_1 and R_2 are methyl.
3. Compound according to Claim 1 or 2, characterized in that R_4 is a direct bond.
4. Compound according to one of Claims 1 to 3, characterized in that R_5 and R_3 are hydrogen.
5. Compound according to one of Claims 1 to 4, characterized in that R_6 , R_7 , R_8 and R_9 are independently hydrogen, chlorine, bromine, methoxy, ethoxy, phenoxy, $-\text{NH-C}_6\text{H}_4\text{-OCH}_3$, $-\text{O-C}_6\text{H}_4\text{-OCH}_3$ or $-\text{S-C}_6\text{H}_4\text{-OCH}_3$.
6. Process for preparing a compound according to one of Claims 1 to 5, characterized in that a dicarboxylic acid of the formula (II)



or one of its functional derivatives is condensed with an amine or the salt of an amine of the formula (III)



7. Process according to Claim 6, characterized in that the functional derivative of the dicarboxylic acid is the acid

anhydride or acid chloride.

- 5 8. Use of a compound according to one of Claims 1 to 5 for coloring synthetic polyamides, polyesters, ABS or polycarbonates and as a colorant in electrophotographic toners and developers, in powder coating materials and in ink-jet inks.
9. Use according to Claim 8 for mass-coloring polycondensates of dicarboxylic acids and diamines, of lactams or of aminocarboxylic acids.

10

15

20

25

30

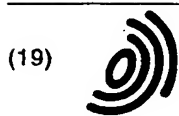
35

40

45

50

55



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 999 239 A3**

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:
06.03.2002 Bulletin 2002/10

(51) Int Cl.7: **C09B 57/14, C09B 57/08**

(43) Date of publication A2:
10.05.2000 Bulletin 2000/19

(21) Application number: **99811010.0**

(22) Date of filing: **04.11.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• Kaul, Bansi Lal
4105 Biel-Benken (CH)
• Piastra, Bruno
68330 Huningue (FR)
• Graciet, Jean Christoph
68330 Huningue (FR)

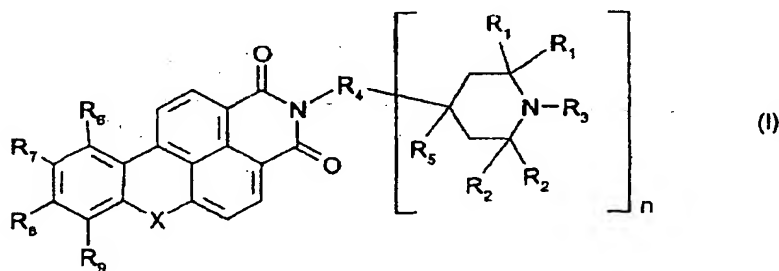
(30) Priority: **06.11.1998 GB 9824314**

(71) Applicant: **Clariant Finance (BVI) Limited**
Road Town, Tortola (VG)

(74) Representative: **D'haemer, Jan Constant**
Clariant International Ltd., Rothausstrasse 61
4132 Muttenz 1 (CH)

(54) **Heterocyclic compounds**

(57) Compounds of the formula (I)



in which the substituents are as defined in claim 1
are valuable colorants for the mass coloring of polymers, with fluorescence property, in electrophotographics toners and developers, in powders coating materials and ink-jet inks.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 81 1010

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	FR 2 137 732 A (HOECHST AG) 29 December 1972 (1972-12-29) * page 2; figure 3 * * page 3, last paragraph - page 4, paragraph 1 * * page 9; example 6 * ---	1-9	C09B57/14 C09B57/08
Y	EP 0 241 419 A (SANDOZ AG ;SANDOZ AG (DE); SANDOZ AG (AT)) 14 October 1987 (1987-10-14) * abstract * * page 7, paragraph 2 - page 8, last paragraph * * page 19, line 2 - last line * ---	1-9	
Y	US 4 902 787 A (FREEMAN HAROLD S) 20 February 1990 (1990-02-20) * abstract; example 8 * ---	1-9	
Y	FR 2 672 054 A (SANDOZ SA) 31 July 1992 (1992-07-31) * abstract; examples 31-35 * ---	1-9	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
A	WO 96 17012 A (MINNESOTA MINING & MFG) 6 June 1996 (1996-06-06) * abstract * ---	1-9	C09B
P,A	WO 99 20688 A (MINNESOTA MINING & MFG) 29 April 1999 (1999-04-29) * abstract * * page 9, line 9 - line 18 * ---	1-9	
A	FR 2 416 251 A (HOECHST AG) 31 August 1979 (1979-08-31) * page 1, last paragraph - page 2, line 16 * * --- -/-	1-9	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 8 January 2002	Examiner Dauksch, H
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03/82 (p.0/01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 81 1010

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 279 (C-257), 20 December 1984 (1984-12-20) & JP 59 147054 A (SUMITOMO KAGAKU KOGYO KK), 23 August 1984 (1984-08-23) * abstract *	1-9	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 8 January 2002	Examiner Dauksch, H
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	

EPO FORM 1503 03 82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 81 1010

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-01-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2137732	A	29-12-1972	DE 2122975 A1	30-11-1972
			CH 569766 A5	28-11-1975
			FR 2137732 A5	29-12-1972
			GB 1391324 A	23-04-1975
			IT 955308 B	29-09-1973
EP 0241419	A	14-10-1987	DE 3612148 A1	10-12-1987
			DE 3618216 A1	03-12-1987
			DE 3630717 A1	17-03-1988
			DE 3632039 A1	31-03-1988
			DE 3638763 A1	26-05-1988
			AT 89587 T	15-06-1993
			DE 3785881 D1	24-06-1993
			EP 0241419 A2	14-10-1987
			ES 2054699 T3	16-08-1994
			HK 73096 A	03-05-1996
			JP 2637731 B2	06-08-1997
			JP 63006058 A	12-01-1988
			US 4838943 A	13-06-1989
			US 4866113 A	12-09-1989
US 4902787	A	20-02-1990	CA 1325007 A1	07-12-1993
			WO 8910384 A1	02-11-1989
FR 2672054	A	31-07-1992	CH 684194 A5	29-07-1994
			DE 4200959 A1	30-07-1992
			FR 2672054 A1	31-07-1992
			GB 2252976 A ,B	26-08-1992
			IT 1254566 B	25-09-1995
			JP 3118477 B2	18-12-2000
			JP 4342767 A	30-11-1992
			US 5304244 A	19-04-1994
WO 9617012	A	06-06-1996	AU 700888 B2	14-01-1999
			AU 3834195 A	19-06-1996
			CN 1168684 A ,B	24-12-1997
			DE 69515062 D1	16-03-2000
			DE 69515062 T2	14-09-2000
			EP 0794975 A1	17-09-1997
			JP 10510313 T	06-10-1998
			WO 9617012 A1	06-06-1996
			US 5605761 A	25-02-1997
			US 5816238 A	06-10-1998
WO 9920688	A	29-04-1999	US 6110566 A	29-08-2000
			AU 6666098 A	10-05-1999

EPO FORM P4589

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 81 1010

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-01-2002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9920688	A		CN 1278841 T	03-01-2001
			EP 1025156 A1	09-08-2000
			JP 2001520293 T	30-10-2001
			WO 9920688 A1	29-04-1999
			US 2001046607 A1	29-11-2001
FR 2416251	A	31-08-1979	DE 2804530 A1	09-08-1979
			BE 873939 A1	06-08-1979
			BR 7900648 A	28-08-1979
			CH 640254 A5	30-12-1983
			FR 2416251 A1	31-08-1979
			GB 2028359 A , B	05-03-1980
			IT 1110296 B	23-12-1985
			JP 54114332 A	06-09-1979
			NL 7900880 A	07-08-1979
			US 4242139 A	30-12-1980
JP 59147054	A	23-08-1984	JP 1776241 C	28-07-1993
			JP 4066907 B	26-10-1992

EPO FORM P0458

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82